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EUROPEAN PATENT APPLICATION (12)

ล้ายกับ โดย เป็น คาวา แบบอากั นาย published in accordance with Art. 158(3) EPO การเดียงาน การคราว คาวา (การเดียง day wells to particular the present invegrior relates to an injurovement of durisary rosistance to the energy south of (43) Date of publication: 5 oral and 5 hs. (10) seed abroadio (51) int cl.7: C22C 38/00, C22C 38/58;

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With the state of th (22) Date of filing: 18.06.2003 Manager bedotsvet many vitreous PCT/JP2003/007709 chanda aswirctor to mamage done with increase of crude oil price and anticipated oil resource depleton in the user future. These oil victioned grisnerreita a contractiva orularegmei-dout a la inemporaria (87), International publication number: el alle enco alleva மைச் டி. முழ் ட்டு நடிய குற்றாடி சுப்பும் படுமுறை நடிய தவுள் நவுக் yigh WO 2004/001082-(31,12,2003, Gazette 2004/01)

:(84)::Designated:Contracting:States::elins:: others from Tayer TAMARI, Takanori, OD vidoid (are not to 780):01 week yHUdE IT.LI LU MCdNLdPT ROSSE SISKSTRo D≥00 than a Chiyoda-kuaTokyo 100-0011 (JP) to che di tsaw sesinists esergional antitylotenum in the consistent resistance of partitude of the two-data as a consistent resistance of the consistent resistance of the consistent resistance of the consistent resistance of the consistent resistance of t -(30) sPriority:v49.06:2002e JPs:2002178974/ tort out houbs that and/osJFE/STEELsCORPORATION:sind classified leads asupaga tervise18.04:2003; JPp2003/1/4775idastow tod by puber Chiyoda,ku,sTokyo,100-001/a(JP) Letro herufostu expensive Accordingly ar merper sive 196-Or martens in stainings si46234(5002); Accordingly are merper consistent in significant as a second and a second and a second are second as a sec www.io i and realth out aC ibertaeb apports resoured config. (7.4) Representative: Grünecker, Kinkeldey, a signived (7.1) Applicant: JFE Steel Corporations yipmbroson bod Tokyo, 100-0011 (JP)

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Tax AT-BE BG, CH CY, CZ-DE;DK:EE/ES:FI FR GB, GR / principle of clo JFE STEEL/CORPORATION (1966-2019) 2 280 Jylio/Stockmair & Schwanhäusser Anwaltssozietätab Maximilianstrasse,58 of notificial rich reason resto FOODE. To the so doments (EC) neighbright 80538 stains as stepts for stee pipes) based on this Continuens in the Continuent of the Continu 28 W 518 Jan 1915 (845 monst in a particular transfer of the content American Health and Service No. 8-720M5 has disclosed a matrice for manufacture.

element selected from the group consisting of Zif B, and

W; or carsingly or in combination. Preferably, the steel

'pipe has a martensitic structure containing 5 to 25 per-

cent by volume of a residual austenite phase, or further

Containing 5% percent by volume or less of a femite

phase. Thus, the resulting stainless steel pipe for foil

้เอ็บที่ให้รู้ในไว้นี้เล็ก goods exhibits ลี ริ่นอุฮีกิดี corrosion re-

"sislance even in extremely severe corrosive environ-

"ments containing carbon dioxide gas (CO2), chloride

₹(54)™STAINLESS=STEEEPPIPEFOR:0IE:WEEEEAND/PROCESS=FOR-PRODUCING-THE:SAME® @# 13%-Or madensitic stainless steel pipe, the Cicontent is limited to the range of 0.005% in 0.05% 2.4% to 6% or 6%

A steel composition contains: 0.05% or less of the formation point or less. The composition may further C; 0.5% or less of Si; 0.20% to 1.80% of Mn; 0.03% or Philippointain at least one element of Nb and Ti; at least one less of P; 0.005% or less of S; 14.0% to 18.0% of Cr 5.0% to 8.0% of Ni; 1.5% to 3.5% of Mo; 0.5% to 3.5% of Cu; 0.05% of less of Al; 0.20% of less of V; 0.01% to 0.15% of N; and 0.006% or less of O on a mass basis, and satisfies the following expressions: Cr + 0.65Ni 7 0.6Mo + 0.55Cu - 20C ≥ 18.5 and Cr + Mo + 0.3Si - 43.5C - 0.4Mn - Ni - 0.3Cu - 9N ≤ 11 (Where Cr. Ni, Mo, Cu, C. Si, Mn, and N represent their respective contents (mass%)). After such a steel pipe material is formed into 의 lons (Cl-) , of the like the 나는 아들이 가려고 하는 사람들 등이 없어. a steel pipe, the steel pipe is quenched by cooling after o heating to a temperature of the Acs transformation point to All poewied stutered multiple and a temperature of the Acs transformation point then cooled to a temperature of the Act and temperature of the Act transfer and temperature of a temperature of the Act transfer and temperature of the Act transfer and temperature of the Act transfer and the act to the temperature of the Act transfer and the act to the temperature of the Act transfer and the act to the temperature of the Act transfer and the act to the temperature of the Act transfer and the act to the transfer and the act to the transfer and the act to the transfer and the transfer and the act to the transfer and the transfer

to the metind indicaters acrosion cracking resistance is remarkably enhanced by forming in marginalist statetare cominating 20 percent by volume or leaded by phase

Facts as a manager of the contract of the placetion Publication No. 17.12 and an arranger of the contraction contributed to 15% of Octobrook spiritual considerations residence and sufficience or respiration of the firm The mail including tambers seed has a composition in which the Origoniant is set at 10% to 15% the Origonian is timited to be a control of 0.05% to 1.05% at 0% or more of Ne and 0.5% to 3% of Ou are indified in control to the to 3,0°C of More stides stided. Furthermore is at the nominalison is set at 10 or not a 17% sinustric of a contraction parties on a confere planner ad maden, the page of the half he present and the exidual authorities of the control percentage of the termoned marketailte ween and the market phase elect the range of Eline in the continue מסיניושוב והנכיויקצונות בירת בנולוקלת נודמים בשחתמום בהפנואותן רסב נובחבריות ביווו החונית שימטירי אים

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Description

Technical Field

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[0001] The present invention relates to steel pipes for oil country tubular goods used in crude oil wells and natural gas wells. In particular, the present invention relates to an improvement of corrosion resistance to extremely severe, corrosive environment in which carbon dioxide gas (CO₂), chloride ions (Cl⁻), and the like are present.

Background Art

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16-03.200s - Bulletin 2003/11

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[0002] Deep oil wells, which have not conventionally been regarded at all, and corrosive sour gas wells, the development of which was abandoned for a time, have recently been developed increasingly on a world scale in order to cope with increase of crude oil price and anticipated oil resource depletion in the near future. These oil wells and gas wells generally lie at great depths in a severe, corrosive environment of a high-temperature atmosphere containing corrosive substances, such as CO₂ and Cl. Accordingly, steel pipes for oil country tubular goods used for digging such an oil or gas well have-to be highly strong and corrosion-resistant.

[0003] In general, highly CO2/corrosion-resistant 13%-Cr martensitic stainless steel pipes are used in oil wells and gas wells whose atmospheres contain CO2. Cl., or the like. However, conventional martensitic stainless steels cannot wear in environments at high temperatures of more than 100°C containing a large amount of Cl. Accordingly, two-phase stainless steel pipes are used in oil wells requiring corrosion resistance. Unfortunately, the two-phase stainless steel pipes contain large amount of alloying elements to reduce the hot workability? Consequently, they must be manufactured only by special heat treatment due to their reduced hot workability; and besides, they are disadvantageously expensive. Accordingly, an inexpensive 13%-Cr martensitic stainless steel based pipel for oil country tubular goods having a superior hot workability and CO2 corrosion resistance has been strongly desired. On the other hand, oil well development in cold districts has recently become active, and, accordingly, superior toughness at low temperatures is often required in addition to high strength limited.

[0004] To these demands, improved martensitic stainless steels (or steel pipes) based on a 13%-Cr martensitic stainless steel (or steel pipe), having an enhanced corrosion resistance have been proposed in, for example, Japanese Unexamined Patent Application Publication Nos. 8-120345, 9-268349, and 10-1755, and Japanese Patent Nos. 2814528 and 3251648.

[0005] Japanese Unexamined Patent Application Publication No. 8-120345 has disclosed a method for manufacturing a seamless martensitic stainless steel pipe having a superior corrosion resistance? For a steel composition of a 13%-Cr martensitic stainless steel pipe, the C content is limited to the range of 0.005% to 0.05%, 2.4% to 6% of Ni and 0.2% to 4% of Cu are added in combination, and 0.5% to 3% of Mo is further added. Furthermore, Nieq is set at 10.5 or more. This steel material is subjected to hot working, subsequently cooled at air-cooling speed or more, and then tempered. Alternatively, after being cooled, the steel material is further heated to a temperature between A_{C3} transformation point +10°C and A_{C3} transformation point + 200°C, or a temperature between A_{C4} transformation point and A_{C3} transformation point, subsequently cooled to room temperature at air-cooling speed or more, and then tempered. According to this method, a seamless martensitic stainless steel pipe is achieved which has a high strength of the grade API-C95 or grater, corrosion resistance in environments at 180°C or more containing CO₂, and SCC resistance.

[0006] Japanese Unexamined Patent Application Publication No. 9-268349 has disclosed a method for manufacturing cooled a method for man

ing a martensitic stainless steel having a superior stress-corrosion cracking resistance to sulfides. In this method, a steel composition of a 13%-Cr martensitic stainless steel contains 0.005% to 0.05% of C, 0.005% to 0.1% of N, 3.0% to 6.0% of Ni, 0.5% to 3% of Cu, and 0.5% to 3% of Mo. After hot working and being left to cool down to room temperature, this steel material is heated to a temperature between (A_{C1} point + 10°C) and (A_{C1} point + 40°C) for 30 to 60 minutes, then cooled to a temperature of Ms point or less, and tempered at a temperature of A_{C1} point or less. Thus, the resulting steel has a structure in which tempered martensite and 20 percent by volume or more of γ phase are mixed. According to this method, the sulfide stress-corrosion cracking resistance is remarkably enhanced by forming a martensitic structure containing 20 percent by volume or more of γ phase.

[0007] Japanese Unexamined Patent Application Publication No. 10-1755 has disclosed a martensitic stainless steel containing 10% to 15% of Cr, having a superior corrosion resistance and sulfide stress-corrosion cracking resistance. This martensitic stainless steel has a composition in which the Cr content is set at 10% to 15%; the C content is limited to the range of 0.005% to 0.05%; 4.0% or more of Ni and 0.5% to 3% of Cu are added in combination; and 1.0% to 3.0% of Mo is further added. Furthermore, Ni_{eq} of the composition is set at -10 or more. The structure of the martensitic stainless steel contains a tempered martensitic phase, a martensitic phase, and a residual austenitic phase. The total percentage of the tempered martensitic phase and the martensitic phase is set in the range of 60% to 90%. According to this disclosure, corrosion resistance and sulfide stress-corrosion cracking resistance in environments where wet

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carbon dioxide gas or wet hydrogen sulfide is present are enhanced; on and least the constitution notion of the

[0008] Japanese Patent No. 2814528 relates to an oil well martensitic stainless steel product having a superior sulfide stress-corrosion cracking resistance. This steel product has a steel composition containing more than 15% and 19% or less of Cr, 0.05% or less of C; 0.1% or less of N, 3.5% to 8.0% of Ni, and 0.1% to 4.0% of Mo, and simultaneously satisfying the relationships: 30Cr + 36Mo + 14Si - 28Ni ≤ 455 (%); and 21Cr + 25Mo + 17Si + 35Ni ≤ 731 (%). According to this disclosure, the resulting steel product exhibits a superior corrosion resistance in severe environments in oil wells where chloride ions, carbon dioxide gas, and a small amount of hydrogen sulfide gas are present.

[0009] Japanese Patent No. 3251648 relates to a precipitation hardening martensitic stainless steel having superior strength and toughness. This martensitic stainless steel has a steel composition containing 10.0% to 17% of Cr, 0.08% or less of C, 0.015% or less of N, 6.0% to 10.0% of Ni, 0.5% to 2.0% of Cu, and 0.5% to 3.0% of Mo. The structure of the steel is formed by 35% or more cold working and annealing and it has a mean crystal grain size of 25 μm or less and precipitates with a particle size of 5 × 10-2 μm or more in the matrix. The number of the precipitates is limited to 6 × 106 per square millimeter or less According to this disclosure a high-strength precipitation hardening martensitic

crystaligrains and less precipitation? The division of No and the allegation to the distribution for the division of No and the distribution of th

stainless/steel in which toughness degradation does not occur can be achieved by forming a structure containing fine

[0010] **However; improved 13%*Crimartensitic stainless steel pipes manufactured by the techniques of dapanese Unexamined (Patent Application Publication) Nos. *8-120345; *9-268349 mand *10-1755 and *dapanese Patent? Nos. 2814528 and 3251648 do not stably exhibit desired corrosion resistance in severe; corrosive environments at temperatures of more than 180°C containing *CO2*; Clr; or the like. *add in all associates a print patient more boddern A (11) [0011] In view of the circumstances of the known arts stated above; the present invention has been achieved. The object of the present invention is to provide an inexpensive, corrosion-resistant stainless steel pipe for oil country tubular goods; preferably a high strength stainless steel pipe for oil country tubular goods; having a superior hot workability and exhibiting a superior *CO2* corrosion resistance even in severe; corrosive environments at temperatures of more than 180°C containing *CO2**, Colimon the tilke, more and containing and another than a superior beach [0012] **The present invention is as follows; a superior and a superior and a superior and beach solutions of the present invention is as follows; and the superior and a superior and another and containing asteel composition comprising, as teel composition comprising, as teel composition comprising,

on a mass basis, 0.05% or less of C/0.50% or less of Si; 0.20% to 1.80% of Mn; 0.03 or less of P; 0.005% or less of S; 14.0% to 18.0% of Cr; 5.0% to 8.0% of Ni; 1.5% to 3.5% of Mo; 0.5% to 3.5% of Cu; 0.05% or less of Ai; 0.20% or less of V; 0.01% to 0.15% of N; 0.006% or less of O and the balance being Fe and incidental impurities. The composition satisfies expressions (1) and (2):

Cr + 0.65Ni + 0.6Mo + 0.55Cu + 20C ≥ 18.5 (1) เดิม เสด - ยอดิเด - พิศ. ศาสมาคา เวล อุมา- เออ ดิมา- เออ ดิมา- เออ JE

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alabd №азыт в по в Сг.т.Мо.т.0.3Si - 43.5С - 0.4Mn - Ni - 0.3Cu - 9N ≤ 11 , очт /И ло стели. (2)

(43) A crethur for manufacturing a seamlers string as are a less for oil countril abutar gouds according to 12cm

(2) A corrosion-resistant stainless steel pipe for oil country tubular goods according to (1) in which the composition of further contains at least one element of 0:20% or less of Nb and 0.30% or less of Tilon a mass basis? A (44)

(3) A corrosion-resistant stainless steel pipe for oil country tubular goods according to (1) or (2) in which the com-Position further contains at least one element selected from the group consisting of 0.20% or less of Zr, 0.01% or less of B, and 3.0% or less of W on a mass basis are applied as a grinuparanem of bodiem A (3))

ালে (4) Acorrosion-resistant stainless steel pipe for oil country tubular goods according to any one of (1) to (3) in which the composition further contains 0.0005% to 0.01% of Caron a mass basis! ত ১০৮০ ে ১৯ ১০ ৪০৮০ ৯০১০ কৈ

(5): A stainless steel pipe for oil country tubular goods according to any one of (1) to (4) and whose structure includes 5 to 25 percent by volume of a residual austenitic phase and the balance being a martensitic phase.

(6) A corrosion-resistant stainless steel pipe for oil country tubular goods according to any one of (1) to (4) and whose structure includes 5 to 25 percent by volume of a residual austenitic phase; 5 percent by volume or less of a ferrite phase, and the balance being a martensitic phase.

(7) 'A method for manufacturing a corrosion-resistant stainless steel pipe for oil country tubular goods including the steel pipe from a steel pipe material having a composition; quenching the steel pipe by heating the steel pipe to a temperature of the A_{C3} transformation point thereof or more and subsequently cooling to room temperature at air-cooling speed or more; and then tempering the steel pipe at a temperature of the A_{C1} and then tempering the steel pipe at a temperature of the A_{C1}.

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transformation point thereof or less. The composition contains, on a mass basis, 0.05% or less of C; 0.50% or less of Si; 0.20% to d.80% of Mn; 0.03; or less of P; 0.005% or less of S; d.4:0% to d.8:0% of Cr; 5.0% to 8:0% of Ni; 0.5% to 3.5% of Mo; 0.5% to 3.5% of Cu; 0.05% or less of Al; 0.20% or less of V; 0.01% to 0.15% of N; 0.006% and or less of O, and the balance being Fe and incidental impurities, and the composition satisfies expressions (1) and add (2)::\(\text{A} \) and \(\text{A} \) and \(\text{A} \) \(

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where Granic Mod CusC, SigMn pand N represent their respective contents to represent their respe

air-cooling speed or more, and the tempering is performed at a temperature in the range of 500 to 630°C.

(10) A method for manufacturing a stainless steel pipe for oil country tubular goods according to any one of (7) to sol (9) in which the composition further contains at least one element selected from the group consisting of 0.20% or recless of Zr. 0.01% or less of B; and 3:0% or less of W one mass basis: ididxe yideta tone b 848 1/38 has 83841/89 (11) A method for manufacturing a stainless steel pipe for oil country tubular goods according to any one of (7) to

(10) in which the composition further contains 0.0005% to;0:01% of Caron a mass basis, and in more of [2:000] (12) A method for manufacturing a corrosion-resistant seamless stainless steel pipe for oil country tubular goods, are including the steps of: forming a steel pipe from a steel pipe material having a composition by hot working; cooling the steel pipe to room temperature at air-cooling speed or more or quenching the steel pipe by: further heating to a temperature of the A_{C3} transformation point thereof or more and cooling to goom temperature at air-cooking

speed or more; and then tempering the steel pipe at a temperature of the Actitransformation point thereof or less. The composition contains, on a mass basis, 0.05% or less of C; 0.50% or less of Si; 0.20% to 1.80% of Mn; 0.03 proordess of P; 0.005% or less of Si;14:0% to 18.0% of Cr; 5.0% to 8:0% of Ni;1:5% to 3.5% of Mo;:0.5% to 3:5% of said Cu;;0:05% or less of Al;:0:20% tordess of V; 0.01% to 0.15% of N;;0.006% or less of O;:and the balance being Fe A randkincidental impurities; and the composition satisfies expressions:(1) and (2): 10 10 30 87 or 30 9. 25 to 3:00 9.

Cr + 0.65Ni + 0.6Mo + 0.55Cu + 20C ≥ 18.5 (1)

 $3.91 \le 0.00 = 1.347 = 140.00 = 140.00$ $Cr + Mo + 0.3Si - 43.5C - 0.4Mn - Ni - 0.3Cu - 9N \le 11$ (2)

where Cr, Ni, Mo, Cu, C, Si, Mn, and N represent their respective contents on a mass% basis.

(13) A method for manufacturing a seamless stainless steel pipe for oil country tubular goods according to (12) in which the composition further contains at least one element of 0.20% or less of Nb and 0.30% or less of Ti on a narrange basis, holdwait throughboods about the composition of the publication about the composition of the publication about the composition of the publication about the composition of the composition of

(14) A method for manufacturing a seamless stainless steel pipe for oil country tubular goods according to (13) in which the quenching includes heating to a temperature in the range of 800 to 1100°C and cooling to room, temperature at air-cooling speed or more; and the tempering is performed at a temperature in the range of 500 to 630°C.

(15) A method for manufacturing a seamless stainless steel pipe for oil country tubular goods according to any oil one of (12) to (14) in which the composition further contains at least one element selected from the group consisting of 0.20% or less of Zr, 0.01% or lessof B, and 3.0% or less of Wilon's mass basis as tentral neither and

one-of:(12)-to-(15):in which the composition further contains 0.0005% to 0.01% of Calonia mass basis uioni and (4) of (1) in one or published shoot of the composition further contains 0.0005% to 0.01% of Calonia mass basis uioni and (4) of (1) in one or published shoot of the contains 0.0005% to 0.01% of Calonia mass basis uioni

whose structure includes 5 to 25 percent by volume of his abstronoitneval and other and the Best Modern Carrying Out the Invention abstract of martensitic phase.

[0013]:at "High strength" in the present invention refers to a strength (yield strength: 550 MRa or more) that conventional 13%-Cr martensitic stainless steel pipes; for oil country: tubular; goods, have and preferably, to: a yield strength of 654 MRa or more; peadus, one should be sent into a mark that a mark the present invention have conducted [0014]; Insorder: to accomplish; the above-described objects, the inventors of the present invention have conducted

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intensive research on the effects of alloying element contents to corrosion resistance in corrosive environments at high temperatures in the range of more than'd 80°C to 230°C containing CO32Cl, or the like, based on the compositions of the improved:13%-Crimartensitic stainless steel pipes of the books and the improved as a children in the improved as a childre [0015] As a result, it has been found that both of a favorable hot workability and a superior corrosion resistance in sévere, corrosive environments can be ensured by reducing the C content to be lower than that of the known/13%-Cr martensilic stainless steels and adding suitable amounts of Ni, Mo, and Cu to adjust alloying element contents; so as Our C 5% to 3 5% to satisfy following expressions (1) and (2): (CORG). The element Gu strangthans the projective factor are considered the steel to prevent from hydranic about tration into the steel thereby enhancing the sulfide stress-compain cracking resistance. This office is absence when (f) (f) Cu content is 0.5% or more. However, a content of the content is 0.5% or more. However, a content of the to reduce the hot worksbilling Accordingly, the Ou contour I limited to the range of 0.5% to 0.6%. Outcough if justice in the range of 0.5% to 2.5%. Cr + Mo + 0.3Si - 43.5C - 0.4Mn - Ni - 0.3Cu - 9N ≤ 11 Al: 0.05% or less [0327]. The element Al has a strong effect of deoxidation, but a content of more than 0.05% negatively at that ு ிwherein Cr. Nij Mo, Gü, டிதெடி Mn and N represent their respective contents (mass%)் Furthermore it has been found that a high strength of 654 MPa or more in terms of yield strength can be ensured. 3200 0 df

[0017] The present invention has been completed based on these findings.

[0017] The reason why the steel compositions are controlled will now be explained. Hereinafter, mass percent is expressed by simply who may be sometimes. It is not a set to see the steel of which is the steel of the s

[0019] The element Si serves as a deoxidizer, and, preferably, its content is 0.05% or more in the present invention. However, a content of more than 0.50% reduces the CO2 corrosion resistance and further reduces the hot workability. Accordingly, the Si content is limited to 0.50% or less. Preferably it is set in the tranger of 0.10% to 0.30%, add as a feet of the content is limited to 0.50% or less. not workability CO3 stress corrosion oracking resistands cotting corrosion resistance suffid%08:4:of:%05:0 :nMacking [0020] The element Mn enhances steel strength Intorder to ensure a strength desired in the present invention; the Mn content has to be 0:20% or more: However, a content of more than 180% negatively affects the toughness (AC) cordingly, the Mn content is limited to the range of 0.20% to 1.80%. Preferably, it is set in the range of 0.20% to 1.00%! [0032] Both the elements Albertande the strength 1808.0 to 0.80% of \$100.00 and the elements Albertande and the strength 1808.0 to 0.80% of \$100.00 and the elements Albertande and the strength 1800.00 and the elements Albertande and the strength 1800.00 and the elements Albertande and the elements and the elements and the elements are the eleme remarkably by tempering at a telalively levil lemberature in the same of 500 to 630°C. This effects also workley workley is a field sampering at a relatively 19.00.00 from the field of th [0021] > The element Phagatively affects the CO2 corrosion resistance; CO2 stress-corrosion cracking resistance; pitting corrosion resistance, and sulfide stress-corrosion cracking resistance; and it is preferable that the P content be reduced as low as possible. However, an excessive reduction of P content increases cost. Accordingly, the P content is limited to 0.03% or less so as to allow industrial production at a low cost and prevent the degradation of CO₂ corresion ాresistanceaCO pstress-corrosion cracking resistance, pitting corrosion resistance, and sulfide stress-corrosion (resist) ance. Preferably, it is set at 0.00% or less, a bine of the seal on 12 to easily a work of word and gritale continues and more [0034] Zr. B. and W each increases the strength and at least one of them may be added if raelino %200.048 libra [0022] **The element S seriously reduces hot workability in manufacture of pipes, and the S content is preferably, as low as possible. A S content of 0:005% or less makes it possible to manufacture pipes through a common process, and therefore; the S content is limited to 0.005% or less // Preferably attricts et late 0.003% of less and rectioned to 0.005% or less // Preferably attricts et late 0.003% of less and rectioned to 0.005% or less // Preferably attricts et late 0.003% of less and rectioned to 0.005% or less // Preferably attricts et late 0.003% of less and rectioned to 0.005% or less // Preferably attricts et late 0.003% of less and rectioned to 0.005% or less // Preferably attricts et late 0.003% of less and rectioned to 0.005% or less // Preferably attricts et late 0.003% of less and rectioned to 0.005% or less // Preferably attricts et late 0.003% of less and rectioned to 0.005% or less // Preferably attricts et late 0.003% of less // Preferably attricts et late of W. the toughness is roduced. Accordingly, the 2r content is preferably limited to 0.20% or %0.8hot %0.4h:nD0 01% [0023] The element Cr forms a protective film on the surface of steel to increase the corrosion resistance, and particularly to increase the CO2 corrosion resistance and CO2 stress-corrosion cracking resistance finthe presentlinvent tion, a Cricontent of 14.0% or more is necessary from the viewpoint of increasing the corresion resistance at high temperatures? However, a content of more than 18:0% reduces the hot workability. Accordingly, the Cr content is limited to the range of 14.0% to 18.0% in the present invention. Preferably, it is set in the range of 14.5% to গ্ৰেচিট্ড লেট্ড them 0.01% increases CaO, and reduces the CO_C corrosing issued and pitting resistant %0.8101 %0.011 Nne OF [0024] The element Ni strengthens the protective film on the surface of steel to enhance the CO2 corrosion resistance and CO2 stress-corrosion cracking resistance; pitting corrosion resistance; and sulfide stress-corrosion cracking resistance. Furthermore, it has the effect of a solid solution strengthening and, accordingly, increases steel strength. These effects are exhibited when the Ni content is 5.0% or more. However, a content of more than 8.0% reduces the

stability of the martensitic structure to decrease the strength. Accordingly, the Ni content is limited to the range of 5.0%

to 8.0%. Preferably, it is set in the range of 5.5% to 7.0%.

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ாழுள், Mort 1.5% to 3:5% முரு நார் மாரு கூரு மாரும் மார் மார் முடியாரு எசும் முறையில் உள்ளார். சிரும் ராய் ஆயிலு ஆயுரா [0025] The element Mo enhances the resistance to pitting by Clr, and a content of 1.5% or more is necessary in the present invention. While a content of less than 1.5% does not efficiently achieve the corrosion resistance in severe, corrosive environments: at high-temperatures; a content of more than 3.5% causes; the formation of δ -ferrite to reduce the hot workability, GO2 corrosion resistance, and CO2 stress-corrosion cracking resistance and increases cost. Accordingly/the Mo; content is limited to the range of 1.5% to 3.5%. Preferably, it is set in the range of 1.5% to 2.5%, and Cu: 0.5% to 3.5% is satisfy to lowing eye, express the end (2). [0026] The element Cu strengthens the protective film on the surface of the steel to prevent from hydrogen-penetration into the steel, thereby enhancing the sulfide stress-corrosion cracking resistance. This effect is achieved when the Cu content is 0.5% or more. However, a content of more than 3.5% allows CuS to precipitate in grain boundaries to reduce the hot workability. Accordingly, the Cu content is limited to the range of 0.5% to 3.5%. Preferably, it is set in the range of 0.5% to 2.5%. TEMP LOSG TO MAIN CAMA BECARMAN. AI: 0.05% or less [0027] The element Al has a strong effect of deoxidation, but a content of more than 0.05% negatively affects the toughness; of the steel. Accordingly, the Al content is limited to 0.05% or less. Preferably, it is set in the range of 0.01% to 0.03%. Disturble and non-time to the latest the following to ARM ARS to districte down a production of 1001 c. The present inventor has been completed well and the continues V: 0.20% or less [0028] 19 The element Vienhances the strength of steel and also has the effect of improving the stress corrosion cracking resistance. These effects are noticeably exhibited when the V content is 0.03% or more...However, a content of more than 0.20% reduces the toughness. Accordingly, the V content is limited to 0.20% or less: Preferably, it is set in theirangerof;0:03%:to:0:08%, learn selfiliation of the strength or of pattern thomato lating to as site. [3100] 0.05% prismotes sensitization at the stage of thempering ducities precence of Millin order to %3th.0:oth-0.0:10.cation [0029] ocThe element N extremely enhances the pitting corrosion resistance. This effect is exhibited when the N content is 0:01% or more. However, a content of more than 0.15% allows the formation of various nitrides to reduce the toughness. Accordingly, the N content is limited to the range of 0.01% to 0.15%. Preferably, it is set in the range of 0.03% to 0.15%, and more preferably in the range of 0.03% to 0.08%. Si: 0.50% or less 10019] The element St serves as a decidor of and order to the other of more seal to %00.0 tion [0030] no The element O is present in oxide forms in steel and negatively affects various characteristics alt is, therefore, preferable to be reduced as low as possible. In particular, an O content of more than 0.006% seriously reduces the hot workability, CO2 stress-corrosion cracking resistance, pitting corrosion resistance, sulfide stress-corrosion cracking resistance; and toughness: Accordingly, the EOI content is limited to 0,006% for less applicance in the material and in 192001 [0031]: an Inthe, present invention; the above-described basic composition may further contain at least either 0:20% or conductive the content is limited to the range of 0.20% to 6.1% of characteristic earthorsest, rockers is sentrated. [0032] Both the elements Nb and Ti enhance the strength and the toughness, and particularly increase the strength remarkably by tempering at a relatively low temperature in the range of 500 to 630°C. This effect is noticeably exhibited when the Nb and Elicontents are 0.02% or more and 0.01% or more prespectively. On the other hand, a Nb content of more than 0:20% and acti content of more than 0.30% reduce the toughness the additions Tithas the effect of improving the stress-corrosion cracking resistance. Accordingly, the Nb content is preferably limited to 0.20% or less, and the Ti is limited to 0.03% or less so as to allow industrial production of a lost and prevent the degrazzelino; (0.05, the thought of the content of [0033] not the present invention; the above-described composition may further contain at least one element selected from the group consisting of 0.20% or less of Zr, 0.01% or less of B, and 3.0% or less of W. toalar and global state. [0034] Zr, B, and W each increases the strength, and at least one of them may be added if necessary: In addition to the effect of increasing the strength, Zr, B, and W can improve the stress-corrosion cracking resistance. These effects are noticeably exhibited when the composition contains 0.01% or more of Zr, 0.0005% or more of B, or 0:1% or more of W. On the other hand; if the composition:contains more than 0.20% of Zr, more than 0.01% of B cormore than 3.0% of W, the toughness is reduced. Accordingly, the Zr content is preferably limited to 0.20% or less; the B content, 0.01% or-less and the: Wicontent; 3:0% for less and child the same of the same and content and c [0035] in In the present invention the composition may further contain 0.0005% to 0.01% of Cattersent in wheleout [0036] eThe element Ga forms CaS:to:fix/the:element S and, thus, to spheroidize sulfide inclusions; thereby, reducing lattice distortion of the matrix in the vicinity of the inclusions to reduce the capability of trapping hydrogen of the inclusions advantageously. This effect is achieved when the Ca content is 0:0005% or more: However, a content of more than 0.01% increases CaO, and reduces the CO₂ corrosion resistance and pitting resistance Accordingly, the Ca content is: preferably_limited to the range of 0.0005% to 0.01% with evaluation and another in the content is: preferably_limited to the range of 0.0005% to 0.01% with evaluation and the content is: preferably_limited to the range of 0.0005% to 0.01% with evaluation and the content is: preferably_limited to the range of 0.0005% to 0.01% with evaluation and the content is: preferably_limited to the range of 0.0005% to 0.01% with evaluation and the content is: preferably_limited to the range of 0.0005% to 0.001% with evaluation and the content is: preferably_limited to the range of 0.0005% to 0.01% with evaluation and the content is: preferably_limited to the range of 0.0005% to 0.01% with evaluation and the content is: preferably_limited to 0.0005% t [0037] In addition to the above-described requirements, the each element content have to satisfy following expressigns: (1) and (2) teaenge! Morebroose the end of the control of the selection of the end accordingly the end as the end of the end Twever a content of more than 8 09' requesting Through which are excluded in the North Contest of the August and Contest of the .40 545 rojas rediente rojante rediente de la como de

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ar many of the series are ceres at the station different for the first of the first of the first of the contract of the first of the fi or in the compartments of MW in all the in highlighted that, into ascome a spiroused that are Digital and see wherein Cr. Ni, Mo, Cu, C, Si, Mn, and N represent their respective contents screens is a consulting to honoris [0038] By adjusting the Cr, Ni, Mo, Cu, and C contents so as to satisfy expression (1), the corrosion resistance in environments at high temperatures up to 230°C including CO2 or Cl is remarkably increased. Also, by adjusting the Cr, Mo, Si, C, Mn, Ni, Cu, and N contents so as to satisfy expression (2), the hot workability is enhanced. In the present invention, P, S, and O contents are significantly reduced in order to enhance the hot workability. However, reducing the P, S, and O contents is not enough to ensure a hot workability sufficient to produce seamless martensitic stainless steel pipes. In order to ensure a hot workability sufficient to make seamless martensitic stainless steel pipes sittis important to extremely reduce the P. S. and O contents, and besides to adjust the Cr. Mo, Si, C, Mn, Ni, Cu, and N Toontents so as to satisfy expression (2). If many and the company of the person of the prison of the interest A (2811)] ন্**0039]**চজThe' balance of the foregoing elements is Fe and incidental impurities কৈ কর্মান করে করে করে করে । পি এটিই) 'তুই [0040] Preferably, the steel pipe of the present invention has a structure comprising 5% to 25% of residual austenite phase on a volume basis and the balance being a martensite phase. Alternatively, the steel pipe of the present invention has a structure comprising 5% to 25% of residual austenite phase; 5% or less of ferrite phase; and the balance being [0054] The seamless ricel place was cut into a lost prechi in prece waisadiamulova no leas ricelandam and the seamless riceland was cut into a lost prechi into a los [0041] Although the structure of the steel pipe of the present invention is essentially composed of the martensite ephase, the martensite phase; preferably, contains 5% to 25% of a residual austenite phase, or further contains 5% or clessiofia ferriterphase; ontaivolumerbasis planting and the proposition of the proposition of the period of the p [0042] an By allowing 5: percent: by: volume of more of residual austenite phase to be present a high toughness can be achieved. However, more than 25 percent by volume of residual austenite phase reduces the strength. Accordingly, it ાંs:preferable that the percentage of the residual austenite phase is set in the range of 5મo 25 percent/by volume?પીત additions in order to enhance the corrosion resistance, it is preferable that 5 percent by volume or less of ferrite phase is allowed to be present. However, more than 5 percent by volume of ferrite phase remarkably reduces the hot workability. Accordingly, it is preferable that the percentage of the ferrite phase is set at:5 percent by volume of less 200] ■[0043]⇒<A method for manufacturing the steel pipe of the present invention will now be described taking at seamless the test was observed to check for the occurrence of pitting and a magnificational quarants and eqiq lests [0044] First, it is preferable that a molten steel having the above-described composition be melted by a conventional steel making process using a converter, an electric furnace, a vacuum melting furnace, or the like, and then formed into a steel pipe material, such as, a billet by a conventional method, such as continuous casting or ingot makingslabbling. Then, the steel pipe material is heated and subjected to hot working to make a pipe by a common manufacturing process, such as that of Mannesmann-plug mill or Mannesmann-mandrel mill. Thus a seamless steel pipe with a desired size is yielded. After pipe making, the resulting seamless steel pipe is preferably cooled to room temperature at air-cooling speed or more.

[0045] The seamless steel pipe having the above-described steel composition can be given a structure mainly composed of a martensite phase by cooling at air-cooling speed or more after hot working. After the cooling at air-cooling speed or more, preferably, quenching is performed in which the steel pipe is heated again to a temperature of the A_{C3} transformation point or more and cooled to room temperature at air-cooling speed or more. Thus, the martensitic structure can be refined and the toughness of the steel can be increased.

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[0046] Preferably, the quenched seamless steel pipe is subjected to tempering by being heated to a temperature of the A_{C1} transformation point or less. By heating to a temperature of the A_{C1} transformation point or less, preferably to 400°C or more, for tempering, the resultant structure comprises a tempered martensite phase, further comprises a residual austenite phase, or still further comprises a small amount of ferrite phase in some cases. Thus, the resulting seamless steel pipe exhibits a desired strength, a desired toughness, and a desired, superior corrosion resistance.

[0047] Only tempering may be performed without quenching.

[0048] The description above illustrates a steel pipe of the present invention taking the seamless steel pipe as an example, but the present invention is not limited to this form. A steel pipe material having the composition within the scope of the present invention may result in an electric welded steel pipe or a UOE steel pipe used as a steel pipe for oil country tubular goods through a conventional process. However, for the electric welded steel tube and UOE steel pipe, it is preferable that, after pipe making, the pipe is quenched by heating the pipe again to a temperature of the

pipe, it is preferable that, after pipe making, the pipe is quenched by heating the pipe again to a temperature of the A_{C3} transformation point or more and cooling to room temperature at air-cooling speed or more, and is subsequently tempered at a temperature of the A_{C1} transformation point or less.

[0049] In the case of a steel pipe having a composition containing at least one element of Nb and Ti, quenching includes heating to a temperature of 800 to 1100°C, and cooling to room temperature at air-cooling speed or more. Also, tempering is preferably performed at a temperature in the range of 500 to 630°C. By subjecting the steel pipe having the composition containing at least one element of Nb and Ti to these quenching and tempering, a sufficient amount of fine precipitates can occur to achieve a high strength of 654 MPa or more in terms of yield strength.

[0050] A quenching temperature of less than 800°C does not sufficiently achieve the effect of tempering to provide a desired strength. On the other hand, a quenching temperature of more than 1100°C coarsens the crystal grains to reduce the toughness of the steel. While a tempering temperature of less than 500°C does not pricipitate a sufficient amount of precipitations, a tempering temperature of more than 630°C remarkably reduces the strength of the steel. a consisted common and it in all engine while it is not remained by a letter of the best engineer yes releasing (Examples): A. New Bosesbon (idiabatical res-GENERAL DON'T CONTRACTOR OF COME GROUP THE SERVICE SERVICE and and the application of while the arms of the control of the co [0051]» The present invention will be further described in detail with reference to Examples. It bosts a second mornage to inciP Stand Otroniants is no landigh to ensure a hot where till it will it produce seamical markenatin stainless significant proof in order to ensure a not workability sufficient to a the remaining of a significant significant significant and a significant signif important to extremely reduce the history of and Cloopydres and his couldn't be Or Mai Gill Oliving N. No. No. Ou and N. [0052] After degassing, each molten steel having a composition shown in Table:1-was:casti into_a:steel ingot of 100 kgf (980 N). The ingot was subjected to:hot working to make a pipe with a model:seamless rolling mill, followed by air cooling to yield a seamless steel pipe with an outer diameter of 3.3 incby a thickness of 0.5 init diameter = 104001 [0053]rii The hot;workability:was:evaluated by visually observing the presence of cracks in the internal and external surfaces of the resulting seamless steel pipe as air-cooled after pipe making. இது காலிக்கும் தமக்களைகள் காய் மாக உண் [0054] The seamless steel pipe was cut into a test piece. The test piece was:heated_at/920°C_for 1-hour and then water-cooled. The test piece was further subjected to tempering at 600°C for 30 minutes. It was ensured that quenching was performed on reach sample at a temperature of its Act transformation point or more and that tempering was performed at a temperature of its A_{C1} transformation point or less. The quench-tempered test piece was machined intoral corrosion, test piece of 3:mm in thickness by 30 mm in width by 40 mm in length; followed by a corrosion test. Some of the steel pipe samples, were subjected to only tempering without quenching. எத்து என்ன எல்லையுட்டு நடிகள்கள் [0055] in the corrosion test, the test-piece was immersed in a test solution being 20% NaOI aqueous solution placed in an autoclave (solution temperature: 230°C; CO₂ gas atmosphere at a pressure of 100 atmospheres) and was allowed to keep for 2 weeks in vide are mere asked sign of the contraction of the second and are second asked to keep for 2 weeks in the second asked to be work at the contract of the second asked to be second a [0056]29:The test piece after the corrosion test was weighed, and the corrosion rate was obtained from the difference between the weight of the test piece before the test and that after the test. The surface of the corrosion test piece after the test was observed to check for the occurrence of pitting with a loupe of a magnification of a times. so eqiq leads [0057] suffine preferreble that a motion sie entered to the control of the preferreble that a motion sie entered to the control of the contro size: making process using a convocal an alactic to take the methog rumace of the disc and then formed signification of patients, such as a foliation as convenience in a such as continuous castegio andormategio siabbing, Their the steel plos mainnaise haated and subjected to second to make a pipe for a componimanuface. tuding princess, such as filat of Management, or mild filation of the order specialized as forcess storights with and streamed through help due to the help at state and and gradulter and president applicable. Copiety at the health share 35 al altricopiing speed or niora min vlinem autoure a navig ed har holisconio indina in consumerate in a private a transista e selectros erillos (2000) posed of a martensite phase by rodling at an ecoting entrol diet not wetking. After the cooling at an-cooling pule is heated again to a temp, nature of the App. and or more profescibly quenching is performed in well the transler matien or injolighment and cooled to room temperati r coding speed or more. Thus, the martensing structure can be rotined and the toughness of the structure income reinpering (4) being heated to a temperature of [0046] Preinting the quenched secreps size topo in the of videselend seed of tologient of tests brideselent and an the April ransformation, prim or less. By houting to a temperal time a seancheo redigui inzada olianaturo balsiono: ation is from the transporting the resistant structure of the certific brases in spirit cases. 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The pies it is onserable that after pipe making, the pipe is coercius nsating the dipalageal ; light language of the And translationalion point of there and cobling to mem to a length of attenupeadus si bas leader and is subsectionity. terrection at a temperature of the Application afron paget a factor [0049] If the case of a casel pipe having a composition and at least one element of No and Till quenching com temperature at art-choing speed or more the time. Ordall's static and secure is at painter saturage of 500 to 630°C. By subjecting the steel plan. All the state of the president of the president of the properties of the state of t condended the second is sufficient a sufficient The commission that the gardnating doding the operation was consider to come in terms of violation of the in the confidence is sufficient to cooperate sections at order to the cooperate

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5		Remarks		Example	Examples	Examples	Examples	Example	Examplés	Example:	Example	i Example	Example	Comparative.	Comparative Example	Comparative Example	Comparative Example	Comparative	ou Comparative Example	Comparative Example	Example
10		ance	Pitting	Good VE	Poop	Good	Good	Good	_Good _	Good	Good	Good	- Good -	Good	duc	Good-	:00 3 :00 3	Bad 55		Bad	Good
15		Corrosion resistance	Corrosion rate (mm/yr)	0.113, 10	0.633 0.102, 25	0.091	0,092,37.pp	0.034 0.091 FT.	0.063	0,061	0.045	0.036	0.044	0.005 0.036 EE		0.162 0.034 0.162	0.132 ³⁰ 38 0.058 (18.55	0.179/a 1.1	0.078 Beestou	0.119	0,107
20		Hot workability	Crack	138 Goods	DAX GOODS IN	328 G00d4	Good	045 Good II		Good	Good	Good	Cood	Good Har		17 [Sood Sto	G00d- 23	Badia	Good	Good	Good
25			Cooling	a Air i a a	a All 00	n Ale to 3	0.00	<u> </u>	0	Air	Air	Air	Air	Alr	0 :	A Second	Air of		Air	Air	Alr
30 - ·	Table 2	Tempering	(°C)	1.9600 Se	1 3,600 at	675600013	1. p 600 0 ea	1 2600 G 28	1.000g 7.1	. 600	009	009	009	83.0 V C	-8	5 ve 000 e3	009 C	1 8 8 0 0 2 8 2 W	009-1-20	009	009
35		ا بر ا	²⁰ Cooling (1) (2) (3) (4) (5) (6)	e a Air ia	4 Alg. 12	4 P AIF S.	Alfred	VIE THE	Aig A	Air .	Air	Air	Air	Air or or	A	Alfra	Alr 2	s Air 10	Air	Air	,
40		Quenching		11 920	920	920	5 920	12 920	920	920	920	1-920	920	920-	920	920	920	1 920	920 <u> </u>	920	•
·45		Sooling after pipe making	1 - (vyu) + 0 3 (2)) - 4. 1 + 0 82 (ki) - 0 8 (wo)	To 38 Alfras Go	0.44 AIG 00	ord Alber on	0.45 Albas 100	ove Alcouro	00 10 All. 155 60	Alteria	Air	Air	Air	0.91 No. 0.00	*C Air 05	Air	O'the O'CS O'D	Bill by B	Air	Air	Air
50		Steel No.	ال (ر) الارادة (ر) 200	g useA d 3	0.05 8 0.3	0.03.0	o oscol	0.048E 0.3	0.05%	.	H		, ;	C 530 E.S		C CSEMI O'S.	0 03v 0 5c	18 0ere	d: ::	O	A
55		Steel pipe No.	Exbur	3.7	2, b	3 0	4 14	2 M	9	,	80	6	10		75	13 0	4 · · ·	15 V	10 1 3 1 de l	17	18

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	[0058] Each example of th	-									•				•					•	
	corrosion rate, and no occun	rence o	of pitt	ting.	Hen	ce, i	t has	s þe	eŋ s	hộw	n th	atth	e st	eel	pipe	s of t	hese	exa	mples	have a	Į.
	superior hot workability and	a supe	rior c	orros	sjoñ	resi	stạn	cê i	ņ a s	eve	re, c	orro	sive	er	viror	men	t at a	high	temp	erature	;
٠.	of 230°C containing CO2. In	n contra	ast, i	comp	ara	tive	exar	mple	es joi	ıtsid	e th	e sc	ope	of	the	presi	ent ir	vent	ion e	xhibited	
5	occurrence of cracks, thus sh				11 ~- '						[43]	•		. * .	k f						
	corrosion resistance. In parti									•		. –		•					_		
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10	(Example 2)	i Te neurodon		<u> </u>	ا إحمدس عد			'	1 m mare m			\ 	 	} *					•		31.
,,,	[0059] After sufficient degr	ecina	A 2C	h me	itan	cta	alh:	avin	;	: ימוחר	nnei	tion	sho	\A/m	in Ta	hla '	S MOI	6 656	et into	o ctoo	
	[0059] After sufficient degraing of 100 kgf (980 N). The i																				
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	of 0.5 in. with a model seam	ž.	•		- !- : ! :	.		بامي	İ	! 				! ~ ~ a	îd T			f	ava al	a in the	,
	[0060] After the pipe making		i	,		٠.		1	•		visu	any.	obs(ervi	ո ց տ	ie pre	esend	ce or	crack	s in ine	
15	internal and external surface	, year		•	_	,		4.1) .,		7	: - 4 1 4			:			· 34
	[0061] The seamless steel					•							1	144	Ŧ			_		_	
	under the conditions shown in	, •••	'	+		•				· ·	•	ŧ	ŧ	. 1	į		•		•		
	piece and subjected to a tens	: 10-2	مو _م ورو ا	~~~ ·			- J* :	ا زرت	t 1733		. כו		: .			-					
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20	test piece by machining, and	wa <u>s s</u>	übje	cted	t <u>o</u> <u>a</u>	corr	osio	n te	st.		1, a ₁ = 1		-		! - a a a						
	[0062] In the corrosion test	i, the te	st pi	ece y	was	imm	erse	ed in	a te	st sç	lutio	bu p	eing	20	% Na	aCl a	dneo	us so	olution	n placed	·
	in an autoclave (solution tem	peratur	e:23	30°C	, <u>C</u> C	₂ ga	s atr	mõs	phei	e at	a pr	essi	irė, d	of-3	Datn	nosph	neres	and	was	allowed	
	to keep for 2 weeks.	ന	, (m	0)	· 3/-		ا معبد سے سے	ا ا محمد هامعام سو	ا مد ا		an ng	GL	(C)	-							
•	[0063] The test piece after	1 1-7	, 4 14	۰ ۱۰۰۰	• • • •			the second of	• •	,	- F T-4		.~,	1 000	- 1						
25	between the weight of the co	rrosion	test	piec	e:be	efore	the	test	tano	tha	t aft	er th	ecte	st.	The	surfa	ce of	the	corros	sion test	2: 1
	piece after the test was obse	rved to	che	ck fo	rthe	OCC	urre	nce	of p	itting	wit	hal	οup	e of	a m	agnifi	icatio	n of	10 tim	es. The)
	results are shown in Table 4.	. 13	3	S		į <u>ā</u>	32	7.5		(1) (2)		10.33	1 6	:5		•					
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	•		Mn	0.34	0.49	0.56	0.41	0.38	0.35	0.44	0.39	0.39	0.40	0.36	0.45	0 4	
			Si	0.19	0.29	0.18	0.31	0.17	0.30	0.25	0.24	0.35	0.30	0.25	0.26	5 5	
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[0064] Each example of the present invention exhibited no occurrence of cracks in the steel pipe surfaces, a low corrosion rate, and no occurrence of pitting. Hence, it was shown that the steel pipes of these examples had a superior hot workability and a superior corrosion resistance in a severe; corrosive environment at a high temperature of 230°C containing CO₂. In contrast, comparative examples outside the scope of the present invention exhibited occurrence of cracks, thus showing a reduced not workability, or exhibited a high corrosion rate; thus showing a reduced corrosion resistance. When the manufacture conditions were outside the preferred ranges as set forth in the present invention, the strength was reduced and, accordingly, a high yield strength of 654 MPa or more was not achieved.

5 8 3 8 8 5 (Example 3) 10 [0065] After sufficient degassing, each molten steel having a composition shown in Table 5 was cast into a steel ingot of 100 kgf (980 N). The ingot was formed into a seamless steel pipe with an outer diameter of 3.3 in. by a thickness of 0.5 in with a model seamless rolling mill. [0066] The hot workability was evaluated by visually observing the presence of cracks in the internal and external surfaces of the resulting seamless steel-pipe, as in Example 1.... The seamless steel pipe was cut into a test piece. The test piece was subjected to quenching and tempering [0067] under the conditions shown in Table 6. It was ensured that quenching was performed on each sample at a temperature of its Aca transformation point or more, and that tempering was performed at a temperature of its Aca transformation point or less. A structure observation test piece was taken from the quench-tempered test piece. The structure observation test piece was etched by aqua regia. The resulting structure was observed with a scanning electron microscope (1000 times), and the percentage of the ferrite phase (percent by volume) was computed with an image analysis system. The percentage of the residual austenite phase was determined by X-ray diffraction. [0068] An ark shaped API tensile test piece was taken from the quench-tempered test piece and subjected to a tensile_test_for_the_tensile_properties_(yield_strength_YS, tensile_strength_TS), as in Example_1._Also, a V-notch test piece (thickness: 5 mm) was taken from the quench-tempered test piece, in accordance with JIS Z 2202, and the Charpy impact test was performed on the V-notch test piece to determine the absorption energy vE 40 (J) at 40°C in accordance with JIS Z 2242. [0069].....Eurthermore, a corrosion-test-piece of 3 mm in thickness-by-30 mm in width by 40-mm in length was taken from the foregoing quench-tempered test piece by machining, and was subjected to a corrosion test, as in Example 2. [0070] 🕏 In the corrosion test, the test piece was immersed in a test solution being 20% NaCl aqueous solution placed in an autoclave (solution temperature: 230°C, CO₂ gas atmosphere at a pressure of 30 atmospheres) and was allowed to keep for 2 weeks: [0071] The test piece after the corrosion test was weighed, and the corrosion rate was obtained from the difference between the weight of the test piece before the test and that after the test. The surface of the corrosion test piece after the test was observed to check for the occurrence of pitting with a loupe of a magnification of 10 times. 001 08 3990 45

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		sitions (m		1.50	2 1.62	2.49	1.57	3. 2.87	9-1-97	1.55		-0.3.(Cu)-		
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		<u> </u>		0,001	0.005	0.001	0.001	0.001	-0.001	-0:	+ (ฟู๊ด) +	(Cr)+-(Mo)+ 0.3 (Si)43.5-(C)	Quenching	
S cano	990	18 G	(T.3)	34 0.02	36 0.01	11 0.02	29 0.02	35- 0.02			5 (Nj) 5 0	16) + 0.3 ((.C.) (.C.)		•
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	rable	Steel	121	38 %	30	3D A	Н Н	BE .	36	3H) Expres	*)(Expres	55.66	ここのト

Table	ပ မ	•		•											
Steel	7040	Cooling	Que	Quenching	Tem	Tempering	Structure	ture	Tensile properties	sile rties	impact property	Hot workabity	Corrosion resistance	sion ance	
pipe No.	No.	pipe- making	Тетр (°C)	Cooling	Temp	Cooling	γ quantity vol%	a quantity vol%	YS	TS	Absorbed energy E ₋₄₀ J	Crack	Corrosion rate (mm/yr)	Pitting	Remark
) - AMara	7	CU Air : 02 (V.890		J (1/Asir	u[2,5501)	30Air)	1.7	; ;	868	1021	80.2	Good	0.109	Good	Example
4 7 7 7 7 7 7 7 7 7 7	- 3A -	Air	- 068	. Air	009	Air	10.9		792-	1047	86.1	Good	-0.107	Good	Example
A3	38	Air	- 890	Air-	- 200	Air	6.3-	E 0	889	1061	83.4	Good	0.111	- Good -	Example
A4	38	Air	.890	Air	909	Air	11.2	7.0	847	1030	85.7	Good	0.112	Good	Example
. A5	30	Air	.068	Air.	550	Air	12.5	9:1 :	820	1035	91.2	Good	0.058	Good	Example
A8.	30	Air	.890	مر . وياد	550	Air	16.3	61	5 12/2 C	974	95.4	Good	0.102	Good	Ехатріе
A7	36	SU Air	890	Air	550	A STATE OF THE STA	22.7	ນ ກ 8 ເ	723	2	15 4 95.9	PooS:	0.039	Good	Example
³ C A8 ∪	30	35 Air 0 36	890	OAIRS	0 1 0	Air	26.3	13.9 ² 1 ¹ 90.1	634 C	915	33,104.3 c) Good	501.0	Good	Example
Ag 0	36	Alroa	890	Air	650	Alf. St.	29.6	1.5% 4 10° 0'	599	3,202,0	3.201 _{esc}	poop (0.037	PooS	Example
3VA10	3.3F	3v Air 0 3.	968	Air	009.0	N. S.	3.2	0.0453	3 666 e	149.0	6.24 LZC	peg .	30.0 . 0.086	Good	ComparativeExample-
. A11	36	Air	890	Air	.550ic	(CAIR)	pone dust	- 127	875	1095	79.3	Good	1.80.179	Man Bad ou	Comparative Example
A12	3Н	Air	890	Air	540	Air	7.3	2.7	827	1046	77.0	Good	0.150	Good	Comparative Example
A13	3A	Air	980	Air	450	Air	1	1	949	1018	37.5	Good	0.124	Good	Example

 γ : residual austenite, α : ferrite (δ)

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[0073] Each example of the present invention exhibited no occurrence of cracks in the steel pipe surfaces, a low corrosion rate, and no occurrence of pitting; hence it was shown that steel pipes of these examples had a superior hot workability. In addition, their structure containing 5 to 25 percent by volume of residual austenite phase, or further containing 5 percent by volume of residual austenite phase, or further containing 5 percent by volume of residual austenite phase, or further containing 5 percent by volume of residual austenite phase, or further containing 5 percent by volume of residual austenite phase, or further containing 5 percent by volume of residual austenite phase, or further containing 5 percent by volume of residual austenite phase, or further containing 5 percent by volume of residual austenite phase, or further containing 5 percent by volume of residual austenite in a severe containing 602. Furthermore, the strength is as high as 654 MPa of more in terms of yield strength YS and the loughness is as high as 601 or more in terms of absorbed energy at 40°C.

[0074] In contrast, comparative examples outside the scope of the present invention exhibited occurrence of cracks, thus showing a reduced corrosion resistance. When the manufacture conditions were outside the preferred ranges as set forth in the present invention; the strength was decreased and accordingly, a highlyfeld strength of 654 MPa or more was not according to a supersognal linear to a second college of the superior of the s

[0075] According to the present invention, a high-strength martensitic stainless steel pipe for oil country fubblar goods can be manufactured at a low cost with stability which has a sufficient corrosion resistance in severe, corrosion to such a sufficient corrosion resistance, thus producing particularly advantageous industrial effects.

1) 「CASE OF 1205」(CASE OF 1205) 「ASE OF 1205」(CASE OF 1205) 「ASE OF 1205] 「ASE OF 12

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Claims

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1. A corrosion-resistant stainless steel pipe for oil country tubular goods having a steel composition comprising on a mass basis:

0.05% or less of C;

0.50% or less of Si;

0.50% to 1:80% of Mn; And Addition of And Addition

0.20% for lesse of V; at net non-contraction of the contraction of the

A method for manufacturing a stantiss algebrigg to object to tubular group according to Claim 8, wherein the question in the manufacturing an approximation of the manufacturing in the manufacturing space or more 2.81 ≤ .702 ± u722.0 ± oM9.0 + iN29.0 ± 12.2 atom in manufaction to 630°C.
 (1) executing space or more 2.81 ≤ .702 ± u722.0 ± oM9.0 + iN29.0 ± 12.2 atom in manufaction to 630°C.

where Cr, Ni, Mo, Cu, C, Si, Mn, and N represent the respective contents thereof on a mass% basis.

2. A stainless steelipipe for oil country tubular goods according to Claim 1, wherein the composition further comprises at least one element selected from the group consisting of 0.20% or less of Nb and 0.30% or less of Ti on a mass and basis? Taludus phospholismolegistics as the selected from the group consisting of 0.20% or less of Nb and 0.30% or less of Ti on a mass are basis? Taludus phospholismolegistics as the selected from the group consisting of 0.20% or less of Nb and 0.30% or less of Ti on a mass are basis? Taludus phospholismolegistics as the selected from the group consisting of 0.20% or less of Nb and 0.30% or less of Ti on a mass are basis? Taludus phospholismolegistics are represented by the selected from the group consisting of 0.20% or less of Nb and 0.30% or less of Ti on a mass are basis. The selected from the group consisting of 0.20% or less of Nb and 0.30% or less of Ti on a mass are basis. The selected from the group consisting of 0.20% or less of Nb and 0.30% or less of Ti on a mass are basis. The selected from the group consisting of 0.20% or less of Nb and 0.30% or less of Ti on a mass are basis. The selected from the group consisting of 0.20% or less of Nb and 0.30% or less of Ti on a mass are basis. The selected from the group consisting to 0.20% or less of Nb and 0.30% or less of Ti on a mass are basis. The selected from the group consisting to 0.20% or less of Nb and 0.30% or less of Ti on a mass are basis. The selected from the group consisting to 0.20% or less of Nb and 0.30% or less of Ti on a mass are basis. The selected from the group consisting to 0.20% or less of Nb and 0.30% or less of Ti on a mass are basis. The selected from the group consisting to 0.20% or less of Nb and 0.30% or less of Ti on a mass are basis. The selected from the group consisting to 0.20% or less of Nb and 0.30% or less of Nb and 0.30% or less of Ti on a mass are basis. The selected from the group consisting the selected from the group consisting the selected from the group consisting the group consi

3.00 Arstainless steel pipe for oil country tubular goods according to Claim 10 62) wherein the composition further are comprises at least one element selected from the group consisting of 0.20% or less of Zr. 0.01% or less of B, and see 13.0% of less of W on a mass basis? In the composition of a second seed and control of the control

4. A stainless steel pipe for oil country tubular goods according to any one of Claims 1 to 3, wherein the composition further comprises 0.0005% to 0.01% of Ca on a mass basis.

	thereof includes 5 to 25 percent by volume of a residual austenite phase and the balance being a martensite phase.	
5	6. A stainless steel pipe for oil country tubular goods according to any one of Claims 1 to 4, wherein the structure or less of a ferrite phase; and the balance being a martensite phase.	
10	7 _{CCF} A method formanufacturing a corrosion-resistant stainless steel pipe for oil country tubular goods comprising the steel pipe to a temperature of the A _{C3} transformation point thereof or more and subsequently cooling to room temperature at air-cooling speed or more; and then tempering the steel pipe at a temperature of the A _{C1} transformation point thereof or less, wherein the composition comprises on a mass basis:	•
15	and an open of the solution o	*. <u>.</u>
	0.03 or less of P;	
20	5.0% to 8.0% of Ni; 1.5% to 3.5% of Mo;	b
	த் எளிரும்து055% toj3,5%;of Cujgat, பாரங்கும் கொள்ள கடிகளை நக்கிக்கு கொள்ளுள்ளது. கொள்கு கணியின் 0.05% or less of Al; 0.20% or less of V;	
25	0.01% to 0.15% of N; 0.006% or less of O, and the balance being Fe and incidental impurities, wherein the composition satisfies expressions (1) and (2):	ر.
	The section (1); Cr + 0.65Ni + 0.6Mo + 0.55Cu + 20C ≥ 18.5	
30		`
	Cr + Mo + 0.3Si - 43.5C - 0.4Mn - Ni - 0.3Cu - 9N ≤ 11 (2), (2),	
35	where Cr, Ni, Mo, Cu, C, Si, Mn, and N represent the respective contents thereof on a mass% basis.	2
	8. A method for manufacturing a stainless steel pipe for oil country tubular goods according to Claim 7, wherein the composition further comprises at least one element of 0.20% or less of Nb and 0.30% or less of Tilon a mass basis.	
40	9. A method for manufacturing a stainless steel pipe for oil country tubular goods according to Claim 8, wherein the quenching includes heating to a temperature in the range of 800 to 1100°C and cooling to room temperature at air-cooling speed or more, and the tempering is performed at a temperature in the range of 500 to 630°C.	7
45	10. A method for manufacturing a stainless steel pipe for oil country tubular goods according to any one of Claims 7 to 9, wherein the composition further comprises at least one element selected from the group consisting of 0.20% or less of Zr, 0.01% or less of B, and 3.0% or less of W on a mass basis.	Ş
	11. A method for manufacturing a stainless steel pipe for oil country tubular goods according to any one of Claims 7 and 10, wherein the composition further comprises, 0.0005% to 0.01% of Calons mass basis as asotroits A . S	
50	12. A method for manufacturing a corrosion-resistant seamless stainless steel pipe for oil country tubular goods, comprising the steps of: forming a steel pipe from a steel pipe material having a composition by hot working; cooling and the steel pipe to room temperature at air-cooling speed or more; or quenching the steel pipe by further heating to	3
55	a temperature of the A _{C3} transformation point thereof or more and cooling to room temperature at air cooking speed or more; and then tempering the steel pipe at a temperature of the A _{C1} transformation point thereof or less, wherein the composition comprises on a mass basis:	ړه
٠	ุงการและสายอุดสายอุดสายอุดสายอุดสายสายสีผิน รายอายาก การ ค.ศ. ค.ศ. ค.ศ. ค.ศ. ค.ศ. เกาะวัน รายวันสาย คาฐโทยาน ผ 0.05% or less of C; เกาะวันสายอุดสายอุดสายอุดสายอุดสายอุดสายอุดสายอุดสายอุดสายอุดสายอุดสายอุดสายอุดสายอุดสายอ	
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	0.50% or less of Si;	
	0.20% to 1.80% of Mn;————————————————————————————————————	term with the term to the term
		A A A B TAIL HOUSE A A CLASSE BUT A PORT OF HE CONTROL OF THE CONT
	0.005% or less of Single	
5	14.0% to 18:0% of Cr; ***	राष्ट्रिक स्थापन के जिल्ला है। जिल्ला के कि जिल्ला है। जिल्ला के कि जिल्ला है। जिल्ला के जिल्ला है। जिल्ला के
	5.0% to 8.0% of Ni;	
	1.5% to 3.5% of Mo;	4
	0.5% to 3.5% of Cu;	
	0.05% or less of Al;	frequency of leterardicizal Phona Chardiffication CPC) or to make nation
10	0.20% or less of V;	I T. PRIOS SEARCHED
		र में कि क्षांत्र में उप्रकाशियों का उत्तरदेवने (बोद्धार्थिक कर कि में कि कि विभिन्न में कि
•	0.006% or less of O, and	19890150 .0088625 715 202
		and wherein the composition satisfies expressions (1) and (2):
	ino batanos bottigiros and inolocita, impantico,	and whorein the composition satisfies expressions (1) and (2).
15	the first care described in lateral and the first days are the	Documentation on the case who gain the the sound of the contraction of the case
	Cr.+,0.65Nj+	0.6Mo.+,0.55Cu + 20C ≥ 18.5 (1);
		Koket Jatasaya Shiman Kehr 1971-2003 Sh
	for the control of th	to the state of th
	Cr + Mo + 0.3Si - 4	วิวาณ (2) ช่วงเรา (คะเวลา เกาะการ์ เปราะการ์ (2) สถายการ์ (3) สถายการ์ (3) (3) (3) (3) (3) (3) (3) (4) (5) (5) (6) (6) (7) (7) (7) (7) (7) (7) (7) (7) (7) (7
20		
20	where Cr Ni Ma Cu C Si Ma and N.	consequent the very entire contents the section of
	where Cr, Nr, Nro, Cu, C, Si, Nrin, and Nr	represent the respective contents thereof on a mass% basis.
	49 A mother for monitoring a complete state of	C. DINCUMENTS CONSIDERED TO BE RELEVANT
	13. A method for manufacturing a seamless stainless in the common terms of the common terms of the common terms.	steel pipe for oil country tubular goods, according to Claim 12,
25	wherein the composition further comprises at least	one element of 0.20% or less of Nb and 0.30% or less of Ti on Less 2002 47 (Kavanara)
25	a mass basis.	09 January, 2002 09.01 02:
		THE PART OF THE PA
	14. A method for manufacturing a seamless stainless	steel pipe for oil country tubular goods-according to Claim 13,
	wherein the quenching includes heating to a tem	perature in the range of 800 to 1100°C and cooling to room
20	i '	tempering is perionmed at a temperature in the range of 500 to
30	630°C.	28 February, 2001 (28.02.02),
		1X97 F/115
		steel pipe for oil country tubular goods-according to any one of
		mprises at least one element selected from the group consisting
	of 0.20% or less of Zr, 0.01% or less of B, and 3.09	% or less of W on a mass basis.
35		
		steel pipe for oil country tubular goods according to any one of
	Claims 12 to 15, wherein the composition further c	omprises 0.0005% to 0.01% of Ca on a mass basis.
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INTERNATIONAL SEARCH REPORT	International application No. PCT/JP03/07709
A. CLASSIFICATION OF SUBJECT MATTER	
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B. FIELDS SEARCHED	710 abel in apos (
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Electronic data base consulted during the international search (name of data base and,	where practicable, search terms used)
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C. DOCUMENTS CONSIDERED TO BE RELEVANT	wainiaak a pong balunkim tokochti
Category* Citation of document, with indication, where appropriate, of the released to the property of the pr	evant passages Relevant to claim N
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Further documents are listed in the continuation of Box C. See patent i	family annex.
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